



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification ⁶ : C10G 45/16, B01J 8/22, C07C 5/03 | A2 | (11) International Publication Number: WO 98/37168 (43) International Publication Date: 27 August 1998 (27.08.98) |
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| (22) International Filing Date: 10 February 1998 (10.02.98) | | |
| (30) Priority Data: 97/1463 20 February 1997 (20.02.97) ZA 98/0586 23 January 1998 (23.01.98) ZA | | (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). |
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(54) Title: HYDROGENATION OF HYDROCARBONS

(57) Abstract

A process for hydrogenating long chain hydrocarbons comprises continuously feeding a feedstock comprising long chain hydrocarbons into a slurry bed comprising a slurry of catalyst particles in a slurring liquid. The slurry bed is contained in a reaction zone and the feedstock enters the reaction zone at a low level. A hydrogenation component is fed continuously into the slurry bed, at a low level. The hydrogenation component is allowed to react with the feedstock, to hydrogenate the feedstock, as the feedstock and hydrogenation component pass upwardly through the bed. Hydrogenated long chain hydrocarbons are withdrawn from the reaction zone at a high level, as a hydrogenated product. Any excess hydrogenation component is withdrawn from the reaction zone at a high level.

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HYDROGENATION OF HYDROCARBONS

THIS INVENTION relates to the hydrogenation of hydrocarbons, in particular long chain hydrocarbons. More particularly, the invention relates to a process for hydrogenating long chain hydrocarbons, and to a catalyst suitable for use in the process.

According to a first aspect of the invention, there is provided a process for hydrogenating long chain hydrocarbons, which process comprises

10 continuously feeding a feedstock comprising long chain hydrocarbons into a slurry bed comprising a slurry of catalyst particles in a slurring liquid, with the slurry bed being contained in a reaction zone and the feedstock entering the reaction zone at a low level;

15 continuously feeding a hydrogenation component into the slurry bed, also at a low level;

allowing the hydrogenation component to react with the feedstock, thereby to hydrogenate the feedstock, as the feedstock and hydrogenation component pass upwardly through the slurry bed;

20 withdrawing hydrogenated long chain hydrocarbons from the reaction zone at a high level, as a hydrogenated product; and

withdrawing any excess hydrogenation component from the reaction zone at a high level.

By 'long chain hydrocarbons' is meant hydrocarbons which are in the liquid phase at the operating conditions of the 5 reaction zone.

While the feedstock can, at least in principle, comprise any hydrogen deficient or unsaturated long chain hydrocarbons, the Applicant believes that it may, in particular, comprise a wax fraction. The wax fraction may, 10 more particularly, be that obtained as a product when a synthesis gas is subjected to Fischer-Tropsch reaction conditions. Typically, such a wax fraction may comply with the following: hydrocarbon molecules containing more than 20 carbon atoms; and a congealing point exceeding 90°C.

15 The feedstock may be in the form of a liquid. In the case where the feedstock is a Fischer-Tropsch derived wax fraction which is normally solid or at least non-fluid at ambient temperature, the feedstock may be at an elevated temperature at which it is fluid. The feedstock may thus 20 be at a temperature between 100°C and 350°C.

The rate at which the feedstock is fed into the reaction zone will depend on the composition and colour of the feedstock, but may be such as to provide a weight hourly space velocity of at least 0,5, typically about 3,0.

25 The hydrogenation component is preferably in gaseous form, and may be a hydrogen gas stream or a gas stream rich in hydrogen. The gas stream may be fed into the reaction zone at such a rate that its superficial velocity through the

slurry bed is at least 1 cm/s; however, the superficial gas velocity through the slurry bed is preferably at least 5 cm/s.

5 The gas stream may thus enter the reaction zone through a gas distributor, sparger pipes or the like located at said low level in the reaction zone, with the slurry bed located above and around the gas distributor. The feedstock may then enter the reaction zone in the slurry bed below or immediately above the gas distributor.

10 The slurring liquid will, at the bottom of the slurry bed, comprise a mixture of unhydrogenated and hydrogenated long chain hydrocarbons, with the slurring liquid composition varying as it passes up the slurry bed. Thus, at the point or zone where the hydrogenated product is withdrawn from 15 the slurry bed, the slurring liquid will comprise mainly hydrogenated long chain hydrocarbons.

20 The reaction zone may thus be provided by a slurry bed reactor, with the gas distributor thus located in or near the bottom of the reactor. A hydrogen feed line will also lead into the bottom of the reactor, eg be connected to the distributor, as will a feedstock flow line. The reactor will then be operated so that a slurry bed/gas interface is located some distance from the top of the reactor, ie so that a gas head or vapour space is provided above the 25 slurry bed. An excess hydrogen gas withdrawal line will then lead from a gas outlet at the top of the reactor so that it is in communication with the head space. A hydrogenated product withdrawal line will lead from the reactor at a level below the level of the interface.

The gas velocity in the vapour space between the slurry bed/gas interface and the gas outlet should be low enough to avoid significant entrainment of slurry or slurry components in the outlet gas. Typically, this can be equal 5 to the superficial gas velocity at the top of the slurry bed, to avoid complicating the reactor design by having to adjust the reactor diameter above the top of the bed. A typical gas velocity in the vapour space is therefore of at least 5 cm/s.

10 The concentration of the catalyst particles in the slurry bed may be between 10 mass % and 50 mass %, based on the total slurry bed mass. The slurry bed may be maintained at a temperature between 180°C and 300°C, while the reaction zone may be maintained at a pressure between 10 atmospheres 15 and 50 atmospheres.

20 Separation of the hydrogenated product from the catalyst particles of the slurry bed can be effected either internally in the reactor or externally thereof, using any suitable particle separation system such as a decanter, hydrocyclone or filter.

Excess hydrogen withdrawn from the top of the reactor can naturally be recycled to the gas distributor. The excess hydrogen may then typically be cooled to below 70°C, recompressed, and reheated to above 100°C, prior to being 25 reintroduced into the reactor.

The reactor walls may be heated by means of a steam jacket in order to control the reactor temperature. For large reactors, it is expected that steam pipes, located inside the reactor, may be used.

The catalyst particles may have a size distribution between 1 and 250 microns, preferably between 30 and 170 microns. The catalyst should preferably not degrade to smaller particle sizes to any significant extent over extended periods of time. For example, less than 10% of particles below 30 microns should preferably be produced during a three month period of operation of the reactor; some variations hereof may be acceptable depending on reactor design, product value, feedstock cost and the cost of catalyst replacement.

Preferably, the catalyst may be that obtained by

- (i) subjecting a slurry, comprising a particulate alumina or silica carrier, a nickel compound as an active component and a solvent for the active component, to a sub-atmospheric pressure environment, thereby to impregnate the carrier with the active component;
- (ii) drying the impregnated carrier in a sub-atmospheric pressure environment; and
- (iii) calcining the dried impregnated carrier, thereby to obtain a hydrogenation catalyst suitable for use in the hydrogenation process.

Thus, according to a second aspect of the invention, there is provided a process for the preparation of a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons, the process comprising

- (i) subjecting a slurry, comprising a particulate alumina or silica carrier, a nickel compound as an active component and a solvent for the active component, to a sub-atmospheric pressure

environment, thereby to impregnate the carrier with the active component;

- (ii) drying the impregnated carrier in a sub-atmospheric pressure environment; and
- 5 (iii) calcining the dried impregnated carrier, thereby to obtain a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons.

Still further, according to a third aspect of the
10 invention, there is provided a process for the preparation of a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons, the process comprising

- 15 (i) preparing a particulate alumina or silica carrier;
- (ii) forming a slurry of the particulate alumina or silica carrier, a nickel compound as an active component and a solvent for the active component;
- (iii) subjecting the slurry to a sub-atmospheric pressure environment, thereby to impregnate the carrier with the active component;
- 20 (iv) drying the impregnated carrier in a sub-atmospheric pressure environment; and
- (v) calcining the dried impregnated carrier, thereby to obtain a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons.

30 The nickel compound may be in the form of nickel nitrate. This compound is water soluble, and the solvent may thus be water.

The sub-atmospheric pressure environment during the impregnation may be at a pressure less than 20 kPa (a), and preferably at a pressure less than 10 kPa (a). Likewise, the sub-atmospheric pressure environment during the drying 5 may be at a pressure less than 20 kPa (a), and preferably at a pressure less than 10 kPa (a). Should the impregnation and drying steps take place at higher pressures, eg at atmospheric pressure, it will have a detrimental effect on the dispersion of the nickel compound 10 and therefore in the metal surface area of the catalyst and on its catalytic activity.

The sub-atmospheric pressure environment can thus be obtained by locating the slurry in a suitable enclosed vessel, and drawing the required sub-atmospheric pressure 15 or vacuum on the vessel.

While the impregnation and drying under sub-atmospheric pressure or vacuum environments or conditions can be effected in two separate or distinct steps, they can, if desired, be effected in a single step, so that the 20 impregnation is effected while the drying takes place.

The drying in said sub-atmospheric pressure environment may be continued until the moisture content of the impregnated carrier is below a predetermined level, eg below 20% by mass. Thereafter, the impregnated carrier may be dried 25 further prior to the calcining and/or the calcining may be effected, under non-sub-atmospheric pressure conditions. The further drying or calcining may be effected by passing a drying medium, eg air, in counter-current fashion over the impregnated carrier.

If desired, the dried impregnated carrier and/or the calcined catalyst can be re-slurried with water and fresh active component, for further impregnation as hereinbefore described. This impregnation may also be effected in a sub-atmospheric pressure environment. The resultant further impregnated carrier can then again be subjected to the drying and calcination as hereinbefore described.

The slurry may be formed by initially dissolving the active component in at least some of the solvent prior to forming the slurry with the carrier, so that formation of the slurry will then involve intimate admixing of the carrier and a solution of the active component.

The resultant catalyst may be washed with a suitable washing medium, eg water, after the calcination, to remove unwanted contaminants, such as nickel, which may have formed on the external surface of the catalyst in the form of a shell of nickel, ie without carrier being present in the shell. This washing is preferably effected with agitation, which may be achieved through boiling of the water in which the catalyst is washed. The water may be changed from time to time to speed up the procedure. Failure to perform this washing step may result in the appearance of small particles of the contaminant in the hydrogenated products.

The calcined catalyst may, prior to use, be reduced, eg by subjecting it to heat treatment under the influence of a reducing gas such as hydrogen.

The carrier may be pretreated prior to forming the slurry thereof with the solvent and the active component. This

pre-treatment may comprise precalcining the carrier prior to slurry formation. This calcination may be effected at a temperature between 200°C and 1150°C, preferably between 400°C and 1100°C.

5 The carrier or support may be that prepared by a spray-drying technique, provided that it has been subjected to the calcination temperature hereinbefore referred to, either during manufacture thereof, or subsequently during pretreatment thereof as hereinbefore described.

10 The carrier may, during preparation thereof, be manipulated to modify its pore size distribution to maximize or at least enhance the dispersion of the active component on the carrier surface, while at the same time maximizing or at least enhancing the diffusion of the large hydrocarbon molecules into and out of the pores of the resultant 15 hydrogenation catalyst, during use in hydrogenerating long chain hydrocarbons.

The manipulation may comprise using pore regulating agents such as polyacrylamide (PAA) or polyvinyl alcohol (PVA) 20 during the synthesis of the silica or alumina.

The manipulation may instead, or in addition, comprise mixing other substances such as carbon black or wax particles or other pore modifying agents with the alumina or silica. This mixing can take place with the alumina or silica either being in a gel phase or being in the form of non-porous nano-particles, prior to the spray drying of 25 such gel or nano-particles to produce the carrier.

The manipulation may instead or in addition comprise calcination of the carrier and/or steaming thereof, in the presence or absence of other chemicals such as ammonia, or calcination followed by steaming followed by calcination.

- 5 The mass % of the active component in the carrier may be between 10% to 45%, typically between 15% to 40%, based on the total combined mass of the carrier and the active component.

10 The invention extends also to a hydrogeneration catalyst when prepared by the process as hereinbefore described, and to a hydrogenated product when produced by a process as hereinbefore described.

15 The invention will now be described in more detail with reference to the accompanying drawings and non-limiting examples.

In the drawings,

FIGURE 1 shows, diagrammatically, a process according to the invention for hydrogenating long chain hydrocarbons, with the process including a slurry bed reactor;

20 FIGURE 2 shows, diagrammatically, a different slurry bed reactor which can be used in the process of Figure 1;

FIGURE 3 shows an enlarged view from the bottom of the sparger of the reactor of Figure 2;

25 FIGURE 4 shows an enlarged three-dimensional view of a portion of the sparger of Figure 3;

FIGURE 5 shows, in respect of some of the hydrogenation catalysts of Examples 1 to 12, the metal dispersion of the active component vs the average pore size of the catalyst;

FIGURE 6 shows, in respect of some of the hydrogenation catalysts of Examples 1 to 12, the catalyst performance vs the total metal area of the active compound in the catalyst;

5 FIGURE 7 shows, in respect of some of the hydrogenation catalysts of Examples 1 to 12, catalyst performance vs average pore size of the catalyst; and

10 FIGURE 8 shows, in respect of some of the hydrogenation catalysts of Examples 1 to 12, catalyst performance vs total metal area of the active compound and the average pore size of the catalyst.

15 Referring to Figure 1, reference numeral 10 generally indicates a process according to the invention for hydrogenating long chain hydrocarbons. The process 10 includes a reactor 12.

The reactor 12 comprises a lower narrow reactor portion 14 of relatively small diameter, flaring into a upper portion 16 of larger diameter. The lower end of the narrow reactor portion 14 is closed off with an end piece 17 while the 20 upper end of the portion 16 is closed off with a roof 18. An apertured gas distributor 20 is located inside the narrow reactor portion 14 at its lower end, with a hydrogen feed line 22 leading into the lower end of the narrow reactor portion 14, below the gas distributor 20.

25 A long chain hydrocarbon feedstock feed line 24 leads into the lower end of the narrow reactor portion 14, immediately above the gas distributor 20. A hydrogenated liquid product withdrawal line 26 leads from the upper portion 16 of the reactor 12, while an unreacted hydrogen withdrawal 30 line 28 leads from the roof 18.

A mixing device in the form of a downcomer 34 is located inside the reactor 12. The downcomer 34 acts to keep the catalyst concentration profile and the temperature profile along the length of the reactor 12 as even as possible.

5 The downcomer 34 comprises a degassing section 36 having a relatively large diameter and located within the upper portion 16 of the reactor 12. The downcomer 34 also comprises a transport section 38 of smaller diameter, and located within the reactor portion 14. The degassing section 36 and the transport section 38 are connected together by means of a flared section 40. The downcomer 34 thus has an open upper end 42 as well as an open lower end 44 of smaller diameter than the upper end 42. The downcomer is thus located within a slurry bed 30 of catalyst particles suspended in long chain hydrocarbons,

10 with the upper end 42 being located below a slurry bed/gas interphase 32.

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In other embodiments (not shown), the transport section 38 and part of the degassing section 36 can be located outside the reactor 12, with the outlet end 44 of the transport section then being located inside the reactor 12.

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In use, a Fischer-Tropsch derived wax fraction having a typical boiling range temperature of up to 500°C, is preheated (not shown) to a temperature of at least 100°C to ensure that it is in liquid form, before being fed continuously into the lower end of the narrow reactor portion 14 to form part of the slurry bed 30. At the lower end of the narrow reactor portion 14, the catalyst particles will be suspended, in the slurry bed 30, in a mixture of hydrogenated and non-hydrogenated long chain hydrocarbons, while towards the upper end of the bed 30, ie

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in proximity to a slurry bed/gas interface 32, the catalyst particles will be suspended in substantially hydrogenated long chain hydrocarbons. The feedstock is introduced into the reactor 12 at such a rate that the liquid hourly space velocity therein is about 3,0.

Hydrogen is continuously introduced into the bottom of the narrow reactor portion 14, along the flow line 22. Sufficient hydrogen is introduced so that the superficial gas velocity through the slurry bed 30 is about 5cm/s.

Sufficient catalyst is used such that its concentration in the slurry bed is between about 10 mass % and about 50 mass %, typically about 35 mass %. The slurry bed is typically maintained at a temperature of about 240°C.

The catalyst particles are typically in the range 30 to 170 microns, and a catalyst as hereinafter described with reference to Examples 1 to 15, can be used.

Unreacted hydrogen separates from the slurry bed 30 at the slurry bed/gas interface 32 enters a head space 33 above the slurry bed 30, and is withdrawn continuously along the flow line 28. This hydrogen can be recycled (not shown).

Hydrogenated long chain hydrocarbon product is withdrawn continuously from the reactor 12 along the flow line 26. The liquid product is separated from the catalyst particles either by means of internal separation (not shown) or by way of external separation (not shown).

The degassing section 36 of the downcomer 34 permits the bulk of the gas bubbles to escape from fluidized slurry

that enters the upper end 42 of the downcomer 34. For this purpose, the diameter of the degassing section 36 is sized such that the downward slurry flow in the degassing section 36 is lower than that of the rise velocity of a selected bubble size. The cross-sectional area of the degassing section 36 is between 2% and 50%, preferably between 6% and 25%, of the cross-sectional area of the reactor at the same level. The vertical height of the degassing section 36 is sized to allow sufficient time for the gas bubbles of a selected size to rise out of the degassing section. This height is typically between 0,229m and 0,609m, preferably between 0,305m and 0,508m. The shape of the degassing section 36 is determined by the shape and configuration of the reactor 12 as well as by the space available inside the reactor. In typical applications, the degassing section 36 is cylindrical but it can instead, for example, be in the form of a rectangular or triangular channel (not shown).

The transport section 38 of the downcomer serves to transport the degassed slurry to a lower point in the reactor 12. The flow of slurry through the downcomer results from the density difference between the partially or completely degassed slurry in the transport section of the downcomer, and the aerated slurry on the outside of the downcomer. Provided that efficient degassing takes place in the degassing section 36, the length and internal diameter of the transport section are the main components of the downcomer which determine the slurry flow rate achievable in the downcomer at a particular set of operating conditions. This is due to the fact that the length and internal diameter of the transport section determine the friction loss in the downcomer. The slurry flow rate achieved in the downcomer is a balance between

the density driving force, provided by the density difference hereinbefore referred to, and the friction loss in the downcomer.

The slurry flow rate inside the downcomer can be between
5 0,5 m/s and 10 m/s, but is preferably between 2 m/s and 5 m/s. Thus, the slurry flow rate in the downcomer should preferably be below about 5 m/s to prevent both erosion of the downcomer and physical degradation of the catalyst in the slurry. The minimum flow rate in the downcomer is such
10 that the upward superficial liquid velocity in the reaction zone of the reactor is sufficient to prevent significant catalyst settling. The upward superficial liquid velocity on the outside of the downcomer can be between 0,5 cm/s and 10 cm/s, but preferably is between 2 cm/s and 4 cm/s.

15 In typical applications, the total length of the transport section of the downcomer can be between 0,3m and 32m, but preferably is between 4m and 15m.

The position of the bottom outlet end 44 of the downcomer is such that impingement of degassed slurry onto the reactor wall or reactor internals is minimized. Such
20 impingement may lead to erosion or physical degradation of the catalyst over a period of time. The position of the downcomer outlet end 44 relative to the gas distributor 20 must be such that even distribution of gas into the slurry bed 30 is not adversely effected.
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Settling of catalyst in the downcomer 34 must be prevented. Thus, the angle of the walls of the section 40 of the downcomer should not exceed the angle of repose of the slurry.

Referring to Figures 2 to 4, reference numeral 50 generally indicates a different slurry bed reactor which can be used in the process 10 of Figure 1.

5 Parts of the reactor 50 which are the same or similar to those of the reactor 12, are indicated with the same reference numerals.

10 Instead of having a gas distributor 20, the reactor 50 includes a gas sparger 52. The sparger 52 typically comprises two concentric ring-like sparger pipes 54, 56, with the pipe 56 being located inside the pipe 54. A gas inlet pipe 58 leads into the outer sparger pipe 54, with the hydrogen feed line 22 connected to the inlet pipe 58. A connecting pipe 60 connects the sparger pipes 54, 56.

15 Each of the sparger pipes 54, 56 is provided with a plurality of downwardly directed gas apertures 62. The gas apertures 62 are thus spaced apart circumferentially along the sparger pipes 54, 56. Around each aperture 62 is provided a length of pipe 64. The apertures 62 serve to provide pressure drop of gas from the sparger pipe 54, 56 into the reactor, while the pipes 64 reduce the velocity of the gas before it enters the slurry bed 30. However, the pipes 64 can be omitted, if desired.

20 The apertures 62 are sized to produce a pressure drop of between 5% and 90% of the reactor pressure drop, preferably between 20% and 40% of the reactor pressure drop.

25 Instead of the apertures 62 being downwardly directed they can, if desired, be upwardly directed. The apertures 62 need also not necessarily be spaced evenly apart

circumferentially along the sparger pipes 54, 56 but any desired arrangement thereof can be used. Additionally, the sparger 52 need not necessarily comprise two concentric sparger pipes 54, 56 but any desired sparger pipe configuration can be used.

The sparger 52 is located close to the end piece 17 of the reactor 50.

In laboratory scale simulations of the process 10, a series of catalysts comprising nickel supported on silica or alumina carriers, were prepared and tested for their performance in the hydrogenation of a wax fraction obtained from a Fischer-Tropsch process. The effectiveness of the catalyst as a wax hydrogenation catalyst is measured by the Saybolt colour of the hydrogenated wax. Thus, the higher the Saybolt colour of the hydrogenated wax, the more effective is the catalyst as a wax hydrogenation catalyst. In each case a similar wax fraction was used.

Testing Procedure

In each test, reduction of the catalyst to be tested was carried out at atmospheric pressure using pure hydrogen (purity of 99,999%) in a fluidised bed at a flow rate of 0,5 litres (normal) per minute. Twenty grams of catalyst was loaded in a glass tube and heated up to the desired reduction temperature over a period of 6 hours. The catalyst was kept at the desired reduction temperature for a period of 16 hours, after which it was allowed to cool down to 100°C, whereafter the hydrogen was replaced with argon. The catalyst was then transferred into 30g molten unhydrogenated Fischer-Tropsch wax under an argon atmosphere and allowed to cool down to room temperature.

At room temperature, the catalyst containing Fischer-Tropsch wax was congealed.

5 500g of the same unhydrogenated Fischer-Tropsch derived wax was loaded into a slurry bed reactor (which thus simulated the reactor 12) equipped with a mechanical stirrer and heated under a nitrogen blanket. The boiling temperature of this wax ranged between 370°C and 500°C. The solid mixture of the externally reduced wax hydrogenation catalyst (20 g) and the unhydrogenated wax (30 g) was added
10 to the reactor, and the slurry bed reactor closed. The reactor was flushed with nitrogen from a cylinder (purity of 99,995%), the pressure increased to 30 bar and the temperature increased to 180°C. The stirrer speed was 320 rpm. Hydrogen was then introduced at a flow rate of 0,8 litres (normal) per minute, and the wax was hydrogenated at
15 180°C for 4 hours. The hydrogenation was terminated by replacing the hydrogen with nitrogen whilst rapidly decreasing the pressure to atmospheric and cooling the system. At approximately 150°C, the reactor was unloaded and the wax filtered through Whatman no. 42 filter paper at
20 130°C under an argon blanket.
25

The colour of the hydrogenated, filtered wax was measured on a Colorgard System/05 (trademark) apparatus manufactured by Pacific Scientific, and the result translated to the corresponding Saybolt number.

Examples 1 to 12, 14 and 15 deal with the preparation of hydrogenation catalysts suitable for use in the hydrogenation process of the invention.

EXAMPLE 1

44,6g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as an active component were dissolved in 50ml distilled water. 50g of Al_2O_3 carrier (Puralox SCCa 5/150) (trade mark) obtainable from Condea Chemie GmbH of Überseering 40, 22297 Hamburg, Germany, were added to this solution, to form a slurry. This slurry was vacuum dried for ~3,5 hours in a rotary evaporator with an oil bath temperature of 75°C and a pressure of 71 mbar(a), so that impregnation of the nickel compound into the carrier is effected simultaneously with the drying. This sample was thereafter further dried in a fluidised bed at 150°C for 1 hour followed by calcining at 300°C for 4 hours. The calcined sample was re-slurried in a solution of 29,7g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 50ml distilled water. The slurry was again impregnated and dried in a rotary evaporator with an oil bath temperature of 75°C and a pressure of 71 mbar(a) for ~3,5 hours. It was further dried in a fluidised bed for 1 hour at 150°C and then calcined in air for 4 hours at 300°C.

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EXAMPLE 2

The preparation of the catalyst of this Example was similar to that of Example 1 except that Puralox SCCa 5/90 (trademark), also obtainable from Condea Chemie GmbH, was used as the carrier or support instead of Puralox SCCa 5/150 (trademark).

EXAMPLE 3

43,8g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved with 43,8g of urea in 250ml distilled water. 50g of Al_2O_3 carrier (Puralox SCCa 5/150) (trademark) were added to the solution. The slurry was then put on the rotary evaporator in a closed system for 12 hours with an oil bath temperature of 80°C. A further solution of 43,8g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 43,8g urea and 250ml distilled water was added to the slurry and the reaction was continued for another 12 hours. A final solution of 43,8g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 43,8g urea and 250ml distilled water was added and the slurry was put on the rotary evaporator under the same conditions for a further 12 hours. The slurry was then washed with distilled water until no more nickel nitrate washed out. The washed slurry was dried on the rotary evaporator at 75 mbar(a) with an oil bath temperature of 75°C. It was further dried in a fluidised bed for 1 hour at 150°C and then calcined for 4 hours at 300°C in air.

EXAMPLE 4

The preparation of this catalyst was similar to that of Example 3 with the following differences:

1. Puralox SCCa 5/90 (trademark) replaced Puralox SCCa 5/150 as the support; and
2. Only one post-addition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was made to the slurry and the slurry was washed with distilled water before the addition.

EXAMPLE 5

The preparation of this catalyst was similar to that of Example 3 except that 38,8g Ni(NO₃)₂.6H₂O and 34,5g urea in 50ml distilled water were added to 50g SCCa 5/150 (trademark) as carrier. The slurry was held under the same conditions as Example 3 for 16 hours. No post additions of Ni(NO₃)₂.6H₂O were made before washing.

EXAMPLE 6

74,3g of Ni(NO₃)₂.6H₂O were dissolved in 50ml of distilled water. 1,5ml HNO₃ (55% by vol) were added to the solution. This was then added to 50g of Aluminium Oxide C (trademark) carrier obtainable from Degussa AG, Geschäftsbererch Anorganische Chemieprodukte, Postfach 110533, D-6000 Frankfurt 11, Federation Republic of Germany. The paste was kneaded for 2 hours at atmospheric pressure and the sample was then oven dried at 120°C overnight. The dried sample was crushed and sieved to between 38 and 150 microns after which it was oven dried for a further 1 hour at 150°C in a fluidised bed followed by calcination for 4 hours at 300°C in air.

EXAMPLE 7

The preparation of this catalyst was similar to that of Example 2, except that the pH of the impregnating solution was adjusted to 2 with nitric acid.

EXAMPLE 8

The preparation of this catalyst was similar to that of Example 2, except that the catalyst was calcined in an oven (not fluidised) for 1 hour at 350°C.

5 EXAMPLE 9

Sipernat 22 (trademark), available from Degussa AG, is a large pore size, large pore volume SiO_2 . 74.36g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 150ml H_2O . 50g of Sipernat 22 was added to the solution and the slurry dried, calcined and reduced according to the procedure described for Example 1.

10 EXAMPLE 10

C500-109 (trademark) is a high surface area, large pore volume SiO_2 support available from Engelhard de Meern B.V., Strijkviertel 67, PO Box 19, NI-3454 ZG De Meern, The Netherlands. The catalyst preparation on C500-109 in this Example was similar to that described in Example 1 except that the amount of H_2O added to form the slurry was greater (175ml in the first and 120ml in the second impregnation steps) due to the high pore volume of the carrier.

20

EXAMPLE 11

The catalyst preparation in this Example and which was also based on C500-109 (trademark) (50Ni/100 SiO_2), was similar to that described in Example 1, except that the first impregnation solution was 74.30g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 150ml H_2O ,

25

while the second impregnation solution was 49.54g Ni(NO₃)₂.6H₂O in 100ml H₂O.

EXAMPLE 12

This catalyst was prepared in the same manner as that described in Example 6, up to the point of drying. In Example 6, the catalyst was dried in an oven and then crushed. In this case, it was diluted with water to a sprayable viscosity and then spray dried in a Niro (trademark) atomiser. Spray dried particles are more spherical and would be more abrasion resistant. The spray dried catalyst was calcined and reduced in a similar manner to that described in Example 1. The reduction temperature was 380°C.

Results

Characterization of the catalysts of Examples 1 to 12, and their performance for Fischer-Tropsch wax hydrogenation, are shown in Table 1. Fischer-Tropsch wax comprises a mixture of long chain saturated and unsaturated hydrocarbons.

In Table 1, 'TPR' means Temperature Programmed Reduction. Also 'Nickel loading' means mass % of Ni added to catalyst, while 'metal dispersion' means the degree to which the Ni is dispersed or distributed in or on the catalytic carrier/support.

CHARACTERIZATION OF THE NICKEL CATALYST

TABLE 1

| EXAMPLE | Nickel Loading (%) | Area (m ² /g) | Pore Volume (ml/g) | Pore Size (Å) | Metal Dispersion (%) | TPR Peak max (°C) | Hydrogenated Wax Colour (Saybolt) | Red. Temp (°C) | Metal (Ni) Surface Area (m ² /g Catalyst) |
|---------|--------------------|--------------------------|--------------------|---------------|----------------------|-------------------|-----------------------------------|----------------|--|
| 1 | 20,3 | 140 | 0,23 | 65,1 | 15,7 | 273;402 | 5 | 380 | 22,3 |
| 2 | 18,4 | 89 | 0,22 | 98,9 | 9,7 | 288;490 | 17 | 380 | 12,8 |
| 3 | 12,7 | 165 | 0,35 | 84,9 | 12,4 | 257;461;531 | 5 | 285 | 11,0 |
| 4 | 16,0 | 117 | 0,26 | 88,9 | 10,2 | 236;312;426 | 14 | 380 | 11,4 |
| 5 | 9,9 | 156 | 0,38 | 97,2 | 16,4 | 306;401;530 | 7 | 380 | 11,3 |
| 6 | 23,0 | 90 | 0,39 | 175,1 | 4,9 | 270;378;514 | 22 | 380 | 8,0 |
| 7 | 21,0 | 76 | 0,23 | 121,1 | 8,5 | 228;406;530 | 16 | 380 | 12,5 |
| 8 | 20,2 | 86 | 0,22 | 102,5 | 11,6 | 222;398;500 | 19 | 425 | 16,4 |
| 9 | 22,0 | 123 | 0,75 | 243,7 | 0,5 | 221;400 | -2 | 380 | 0,5 |
| 10 | 21,8 | 218 | 0,88 | 162,5 | 3,4 | 207;365 | 16 | 380 | 5,2 |
| 11 | 29,6 | 172 | 0,77 | 179,0 | 2,8 | 357 | • 17 | 425 | 6,8 |
| 12 | 18,8 | 76 | 0,47 | 245,8 | 5,7 | 229;416;507 | 15 | 380 | 7,4 |

The following conclusions are evident from Table 1:

5 The dispersion of the active component (nickel) is, strongly, a function of the average pore size of the catalyst, although the nature of the carrier, the total amount of the active component and the specific catalyst preparation method also play a role. This is illustrated in Figure 5, which shows the dispersion of the active component vs the average pore size of some of the catalysts of Examples 1 to 12.

10 The intrinsic activity of metal supported catalysts is a function of the metal area of the active component. This metal area depends on the total amount of active component and on its dispersion. Thus, the metal area of the active component increases with the dispersion of the active component and with the total amount of active component in 15 the catalyst.

20 Thus, normally, the higher the metal area of the active component in a catalyst, the better its performance for the hydrogenation of a Fischer-Tropsch wax. In other words, normally, the higher the metal area of the active component, the higher the Saybolt colour of the Fischer-Tropsch wax as a result of its hydrogenation. The results shown in Table 1, however, do not support this expected behaviour, and are depicted in Figure 6, in which the 25 Saybolt colour of the hydrogenated wax vs the metal area of the active component is plotted.

Fischer-Tropsch waxes which can be hydrogenated comprise a mixture of paraffinic, olefinic and oxygenated long chain hydrocarbons. Typically, the length of these hydrocarbons

is from about C₂₀ up to C₈₀ and higher. Because of this, diffusion of the wax hydrocarbon molecules into and out of the catalyst pores is expected to play an important role in the overall catalyst performance. It is well known by those skilled in the art that the diffusion of these large molecules increases with increasing catalyst pore size.

To ascertain whether the catalyst performance is solely linked to the catalyst pore size, the Saybolt colour of the hydrogenated Fischer-Tropsch wax vs the average pore size of the catalyst was plotted (Figure 7). From Figure 7, it can be seen that there is some correlation between the catalyst performance and its average pore size. Higher pore sizes seems to be linked to a higher wax colour, as expressed in Saybolt units.

It seems, therefore that more than one parameter is responsible for the performance of the hydrogenation catalyst.

To ascertain the importance of both the diffusion and the metal area of the active component in the overall performance of our hydrogenation catalyst, the following correlation, which includes the total metal area of the active component as well as the average catalyst pore size, was developed:

$$\text{Overall Catalyst Performance Factor (OCPF)} = \frac{\text{Total metal area X of the active component}}{\left[\text{Average pore size of the catalyst} \right]^2} \quad \text{Eq (1)}$$

where,

- The overall catalyst performance is measured as Saybolt colour of the hydrogenated wax
- The total metal area of the active component is expressed as m^2 per gram of catalyst.
- 5 - The average pore size of the catalyst is expressed in Armstrongs.

This correlation is shown in Figure 8. Here, it is evident that if both the metal area of the active component and the 10 average pore size of the wax hydrogenation catalyst are taken into account, a correlation with the wax colour is possible.

This thus means that the pore size of the wax hydrogenation catalyst has a dual role. Smaller pore sizes result in 15 higher dispersions, which contribute favourably to the dispersion of the active metal component of the catalyst, and therefore contribute favourably to the overall catalyst performance. Smaller pore sizes, on the other hand, have a negative effect on the catalyst performance due to their 20 negative effect on the diffusion of the wax molecules into and out of the catalyst pores.

An effective long chain hydrocarbon hydrogenation catalyst must therefore preferably be prepared (impregnation of the active component and drying) at sub-atmospheric pressure, 25 and have a careful manipulation of the pore size distribution, with particular emphasis on the amount of small (micropores) and large (macropores) pores. The small pores will ensure a high metal (active component) area while the large pores will facilitate the diffusion of the 30 long chain hydrocarbon molecules.

EXAMPLE 13

A batch of 12kg of the catalyst described in Example 2 was prepared following a similar recipe although on a larger scale. This catalyst was tested in a slurry bed pilot plant reactor 12 with a narrow reactor portion diameter of 5cm and height of 12m. 8kg of catalyst were loaded into the reactor, and the wax to be hydrogenated was fed at a rate of 25kg per hour. Hydrogen was co-fed at a rate of 35m³ per hour and the continuous reaction took place at 10 240°C and a pressure of 30 bar. The catalyst was then separated from the wax by means of a known solid particle separation system.

The upward liquid velocity in the lower reaction portion 14 was calculated at 13 cm/s, while, in the upper reaction 15 portion 16, it was calculated as being 0,4 cm/s. The liquid velocity along the transport section 38 of the downcomer 34 was calculated at about 2m/s.

It is believed that for a successful commercial application 20 of this invention, a Saybolt colour in excess of 15 after 60 days on line and less than 5 ppm of Ni in the filtered, hydrogenated wax, are required. The results obtained in this pilot plant slurry bed reactor test using the catalyst 25 described in Example 2 were a Saybolt colour of between 18 to 20 after 60 days on line and less than 1 ppm of Ni in the filtered wax. This shows that the catalyst has the required overall catalytic performance and mechanical strength to be successfully used in a large scale.

As shown in Table 1, the same catalyst, ie the catalyst of 30 Example 2, gave a Saybolt colour of 17 when tested in the laboratory or micro slurry bed hydrogenation reactor.

Therefore, and in view of the results obtained in the pilot plant slurry bed hydrogenation reactor, the wax hydrogenation catalyst should preferably give a hydrogenated Fischer-Tropsch wax Saybolt number of 17 or 5 higher, when tested in the micro slurry bed hydrogenation reactor.

A good hydrogenation catalyst must therefore preferably have, according to Figure 8, an OCPF equal to or higher than 200 000.

10 To further ascertain the beneficial effect of macropores in the carrier, two carriers were prepared in which the proportion of macropores was increased in one of the carriers without disturbing the proportion of micropores and mesopores present. The preparation of these two 15 catalyst is described below in Examples 14 and 15.

EXAMPLE 14

20 A spraydried alumina support was prepared by adding 100g of Pural SB (trademark) obtainable from Condea Chemie GmbH to 800ml distilled water. The pH was adjusted to 3,7 with acetic acid and the slurry allowed to stir for 2 hours. The pH was then increased to 6,0 with ammonium hydroxide and the viscosity adjusted with 800ml distilled water. The Al₂O₃ gel was then spraydried. The support was calcined in air at 800°C for 16 hours in an oven. A catalyst was 25 prepared from this support in similar fashion to that of Example 1, except that the spraydried support was used instead of Puralox SCCa 5/150 (trademark).

EXAMPLE 15

The preparation of this support and of a catalyst therefrom, was similar to that of Example 14, except as regards the following:

- 5 1. 10g of carbon black (Corax N110) (trademark), obtainable from Algorax (Pty) Limited, J Tallant Road, Deal Party, Port Elizabeth, South Africa were predispersed in 100ml distilled water and then added to the slurry before lowering the pH to 3.7.
- 10 2. The support was calcined in air for 3 hours at 400°C followed by 1 hour at 450°C, 1 hour at 500°C and 8 hours at 800°C. This calcination procedure controlled the combustion rate of the carbon black, creating new pores without breaking up the particles due to too rapid evolution of gases.
- 15

The effect of the carbon black (Corax N110) addition as described in Example 15 is to increase the proportion of macropores without having an effect on the rest of the pore size distribution. The pores with a diameter above 209Å only contribute about 4% of the total pore volume for the catalyst described in Example 14. These large pores (above 209Å), on the other hand, contribute about 16% to the total pore volume for the catalyst described in Example 15.

These catalysts were reduced, as previously described, at 380°C, and tested in the micro slurry bed reactor in the same manner in which the catalysts of Examples 1 to 12 were tested. The wax hydrogenated using the catalyst described in Example 15 gave a Saybolt number 4 units higher than the wax hydrogenated using the catalyst described in Example 14, therefore confirming the beneficial influence of the macropores in the overall performance of the catalyst.

Therefore, if the pore size distribution of the carrier has been manipulated with Pore Modifying Agents (PMA) to increase the amount of macropores, without disturbing the rest of the pore size distribution, the acceptable minimum 5 OCPF could be lower.

The mechanical strength of the catalysts described in Examples 2 and 6 is shown in Table 2. Here, the mechanical strength is measured by means of the Jet Impingement Test. In this test, 100g of the catalyst to be tested is loaded 10 into a feeder. A stirrer located at the bottom of the feeder ensures that a constant flow of catalyst is sucked into a line in which air is fed upstream at a pressure of 2 bar. The air flow impinges a continuous and constant amount of catalyst against a steel plate. The breakage of 15 the catalyst particles upon impingement is directly related to their mechanical strength. The percentage of broken particles is determined by measuring the particle size distribution before and after the jet impingement test by means of a Microtrac ASVR (trademark) manufactured by 20 Leeds+Northrup.

TABLE 2

ATTRITION TEST RESULTS (Jet Impingement)

| | PARTICLE SIZE (microns) | Change in % Fines | |
|---|----------------------------|-------------------|-----------|
| | | Example 2 | Example 6 |
| 5 | 66 | 12,28 | 28,54 |
| | 44 | 7,69 | 23,15 |
| | 22 | 4,00 | 12,45 |
| | 11 | 3,00 | 7,78 |
| | 5,5 | 2,12 | 5,03 |
| | 1 | 0,55 | 1,69 |

The percentual change in the 11 to 22 microns particle range for the catalyst described in Example 2 is 4%, while the same change for the catalyst described in Example 6 is 12,45%. Based on known experience in slurry bed reactors, catalysts which show a percentual change in the 11 and 22 micron fractions of higher than 12%, show a breakage of the catalyst particles under the hydrodynamic conditions experienced in the slurry bed large scale reactors. The breakage percentage of the catalyst described in Example 6 is typical of catalysts in which the carrier is composed by peptised non-porous alumina or silica nano-particles, either spray dried directly to the required particle size or calcined as a cake, followed by crushing to the desired particles size (eg the catalysts whose preparations are described in Examples 6 and 12).

The catalyst described in Example 2 is adequate from a mechanical strength point of view. Therefore, the mechanical strength of the family of catalysts which are part of this invention should preferably be similar or better than that of the catalyst of Example 2.

The hydrogenation of long chain hydrocarbons requires contact thereof with hydrogen in the presence of a solid catalyst. These reactions are more effective when smaller catalyst particle sizes are used although the separation of hydrocarbons from the catalyst is more difficult. It is known that for catalyst particle sizes below approximately 100 microns there is no further significant improvement in reaction rate per unit mass of catalyst.

For particle sizes less than about 2 millimetres it becomes impossible to contain the particles in a static bed of catalyst without encountering very high pressure drops and the catalyst size is usually selected to optimise the pressure drop across the catalyst bed. This results in a typical catalyst pellet size of 2mm or larger for static beds, which results in a poor catalyst utilization due to diffusional limitations. A slurry bed reactor allows the use of much smaller particles, and therefore a more effective and economical catalyst utilization. In a slurry bed reactor, there is a continuous movement of these small catalyst particles with the passage of hydrocarbons and hydrogen through the catalyst bed. This inevitable movement of catalyst particles results in mechanical forces on the particles which tend to further break-up the catalyst to particle sizes below 10 micron which causes the separation of the catalyst from the liquid hydrocarbons to become more difficult.

This invention thus provides

- (i) A method of producing a stronger catalyst with the required size and hydrogenation ability.

-
-
-
-
- (ii) A concept of selecting a catalyst particle size which is a compromise between the optimums for catalyst reaction and solids separation performance
- 5 (iii) Use of a slurry bed reactor for the hydrogenation of long chain hydrocarbons as a continuous process.

CLAIMS

1. A process for hydrogenating long chain hydrocarbons, which process comprises
 - 5 continuously feeding a feedstock comprising long chain hydrocarbons into a slurry bed comprising a slurry of catalyst particles in a slurrying liquid, with the slurry bed being contained in a reaction zone and the feedstock entering the reaction zone at a low level;
 - 10 continuously feeding a hydrogenation component into the slurry bed, also at a low level;
 - 15 allowing the hydrogenation component to react with the feedstock, thereby to hydrogenate the feedstock, as the feedstock and hydrogenation component pass upwardly through the slurry bed;
 - 20 withdrawing hydrogenated long chain hydrocarbons from the reaction zone at a high level, as a hydrogenated product; and
 - 25 withdrawing any excess hydrogenation component from the reaction zone at a high level.
- 20 2. A process according to Claim 1, wherein the feedstock is a wax fraction obtained as a product when a synthesis gas is subjected to Fischer-Tropsch reaction conditions, with the wax fraction comprising hydrocarbon molecules containing more than 20 carbon atoms, and having a congealing point exceeding 90°C.
3. A process according to Claim 2, wherein the feedstock is in liquid form and is at a temperature between 100°C and 350°C, and wherein it is fed into the reaction

zone at such a rate as to provide a weight hourly space velocity of at least 0,5 in the reaction zone.

4. A process according to Claim 2 of Claim 3, wherein the hydrogenation component is in gaseous form, and
5 is a hydrogen gas stream or a gas stream rich in hydrogen, with the gas stream being fed into the reaction zone at such a rate that its superficial velocity through the slurry bed is at least 1 cm/s.

5. A process according to any one of Claims 1 to 4 inclusive, wherein the concentration of the catalyst particles in the slurry bed is between 10 mass % and 10 50 mass %, based on the total slurry bed mass, while the slurry bed is maintained at a temperature between 180°C and 300°C, and the reaction zone is maintained at a pressure 15 between 10 atmospheres and 50 atmospheres.

6. A process according to any one of Claims 1 to 5 inclusive, wherein the catalyst particles have a size distribution between 1 and 250 microns.

7. A process according to Claim 6, wherein the catalyst particles have a size distribution between 30 and 20 170 microns.

8. A process according to any one of Claims 1 to 7 inclusive, wherein the catalyst is that obtained by
25 (i) subjecting a slurry, comprising a particulate alumina or silica carrier, a nickel compound as an active component and a solvent for the active component, to a sub-atmospheric pressure

environment, thereby to impregnate the carrier with the active component;

- (ii) drying the impregnated carrier in a sub-atmospheric pressure environment; and
- 5 (iii) calcining the dried impregnated carrier, thereby to obtain a hydrogenation catalyst suitable for use in the hydrogenation process.

9. A process for the preparation of a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons, the process comprising

- (i) subjecting a slurry, comprising a particulate alumina or silica carrier, a nickel compound as an active component and a solvent for the active component, to a sub-atmospheric pressure environment, thereby to impregnate the carrier with the active component;
- (ii) drying the impregnated carrier in a sub-atmospheric pressure environment; and
- 15 (iii) calcining the dried impregnated carrier, thereby to obtain a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons.

10. A process according to Claim 9, which includes pretreating the carrier prior to forming the slurry thereof with the solvent and the active component, by precalcining the carrier, at a temperature between 200°C and 1150°C.

11. A process for the preparation of a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons, the process comprising

- (i) preparing a particulate alumina or silica carrier;
- (ii) forming a slurry of the particulate alumina or silica carrier, a nickel compound as an active component and a solvent for the active component;
- 5 (iii) subjecting the slurry to a sub-atmospheric pressure environment, thereby to impregnate the carrier with the active component;
- (iv) drying the impregnated carrier in a sub-atmospheric pressure environment; and
- 10 (v) calcining the dried impregnated carrier, thereby to obtain a hydrogenation catalyst suitable for use in a hydrogenation reaction of long chain hydrocarbons.

15 12. A process according to Claim 11, which includes, during the preparation of the carrier, manipulating it to modify its pore size distribution so as to enhance the subsequent dispersion of the active component on the carrier surface.

20 13. A process according to Claim 12, wherein the manipulation of the carrier includes adding a pore regulating or modifying agent to the carrier during the preparation of the carrier.

25 14. A process according to Claim 13 wherein, in the manipulation of the carrier, the pore regulating or modifying agent is mixed with the carrier while it is in a gel phase or in the form of non-porous nano-particles, and thereafter spray drying the gel or nano-particles.

15. A process according to any one of Claims 12 to 14 inclusive, wherein the manipulation of the carrier includes calcination of the carrier and/or steaming of the carrier.

16. A process according to any one of Claims 9 to 15 inclusive, wherein the nickel compound is nickel nitrate which is water soluble, with the solvent being water.

17. A process according to any one of Claims 9 to 16 inclusive, wherein the sub-atmospheric pressure environment during the impregnation is at a pressure less than 20 kPa(a), while the sub-atmospheric pressure environment during the drying is also at a pressure less than 20 kPa(a).

18. A process according to any one of Claims 9 to 17 inclusive, wherein the drying in the sub-atmospheric pressure environment is continued until the moisture content of the impregnated carrier is below 20% by mass, whereafter the impregnated carrier is dried further prior to the calcining and/or the calcining is effected, under non-sub-atmospheric pressure conditions.

19. A process according to Claim 18, wherein the dried impregnated carrier and/or the calcined catalyst is re-slurried with water and fresh active component, and subjected to impregnation in a sub-atmospheric pressure environment, with the resultant further impregnated carrier then being subjected to drying in a sub-atmospheric pressure environment, and thereafter to calcination.

20. A process according to any one of Claims 9 to 19 inclusive, which includes, after the calcination, washing

the catalyst with a washing medium to remove any unwanted contaminants which have formed as a shell on the external surface of the catalyst, with the washing is optionally being effected with agitation.

5 21. A process according to any one of Claims 9 to 20 inclusive, which includes reducing the calcined catalyst by subjecting it to heat treatment under the influence of a reducing gas.

10 22. A process according to any one of Claims 9 to 21 inclusive, wherein the mass percentage of the active component in the carrier is between 10% to 45% based on the total combined mass of the carrier and the active component.

15 23. A hydrogenation catalyst, when prepared by the process of any one of Claims 9 to 22 inclusive.

24. A hydrogenated product, when produced by the process of any one of Claims 1 to 8 inclusive.

20 25. A novel process for hydrogenating long chain hydrocarbons, substantially as described and illustrated herein.

26. A novel process for the preparation of hydrogenated catalyst, substantially as described and illustrated herein.

25 27. A novel hydrogenation catalyst, substantially as described and illustrated herein.

28. A novel hydrogenated product, substantially as described and illustrated herein.

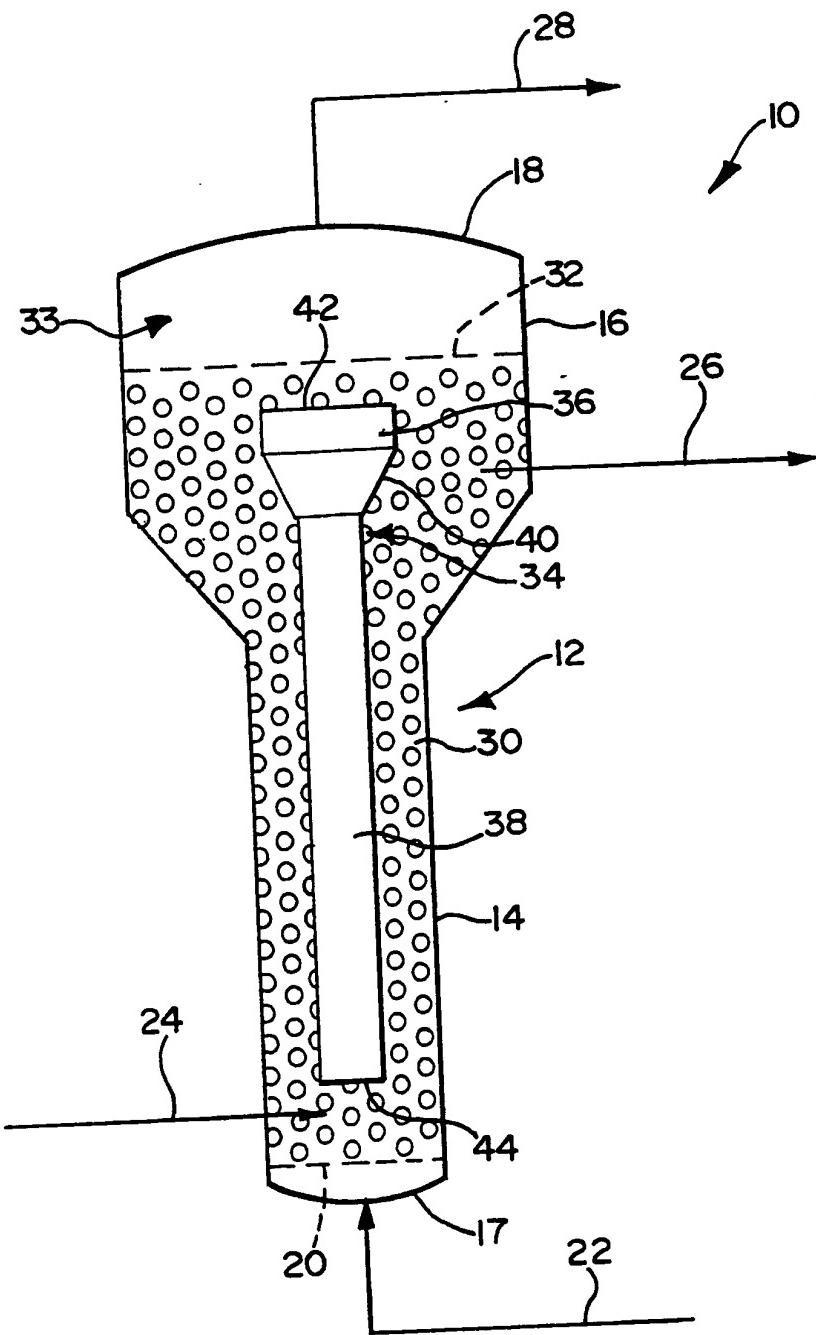


FIG 1

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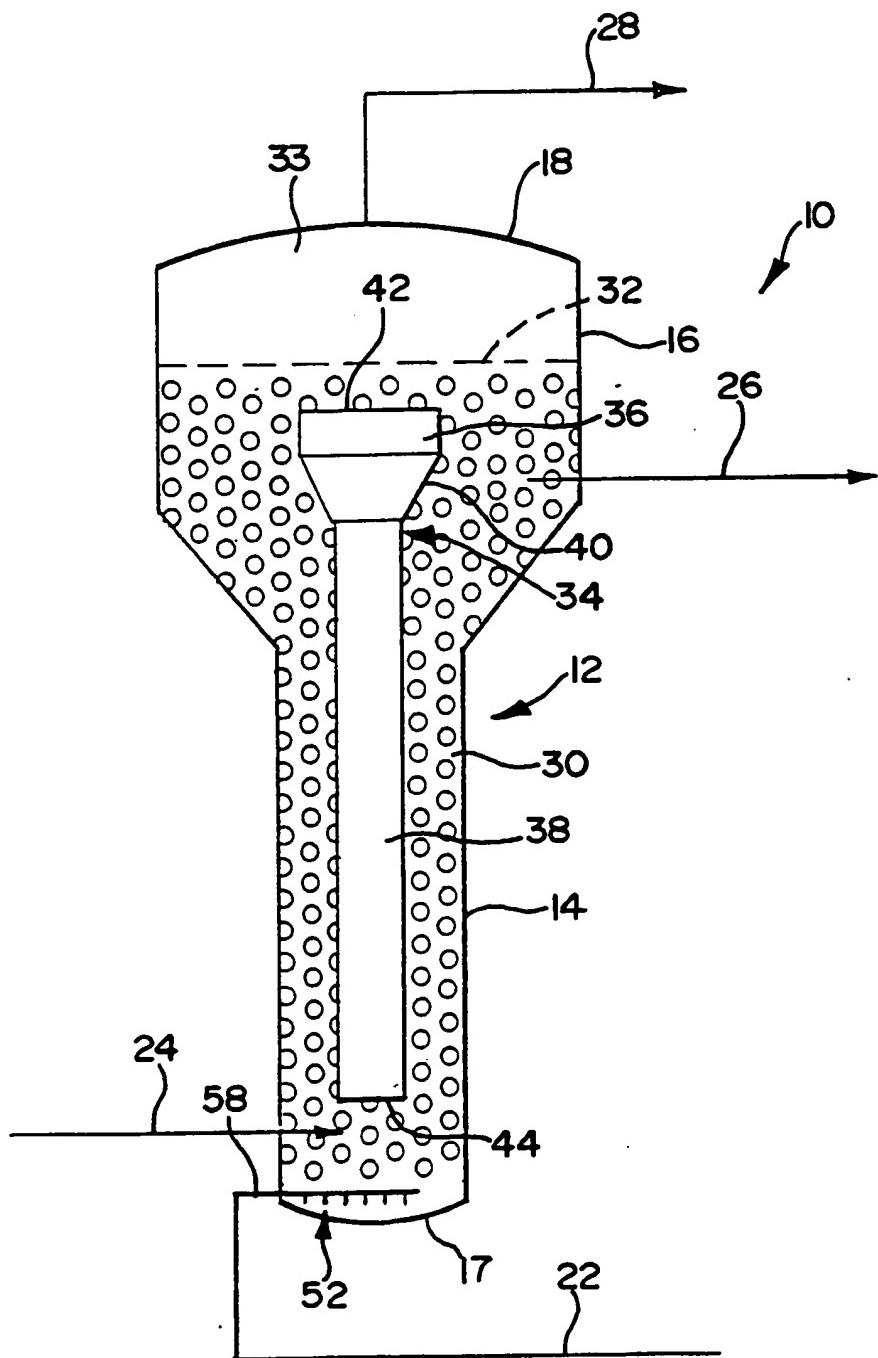


FIG 2

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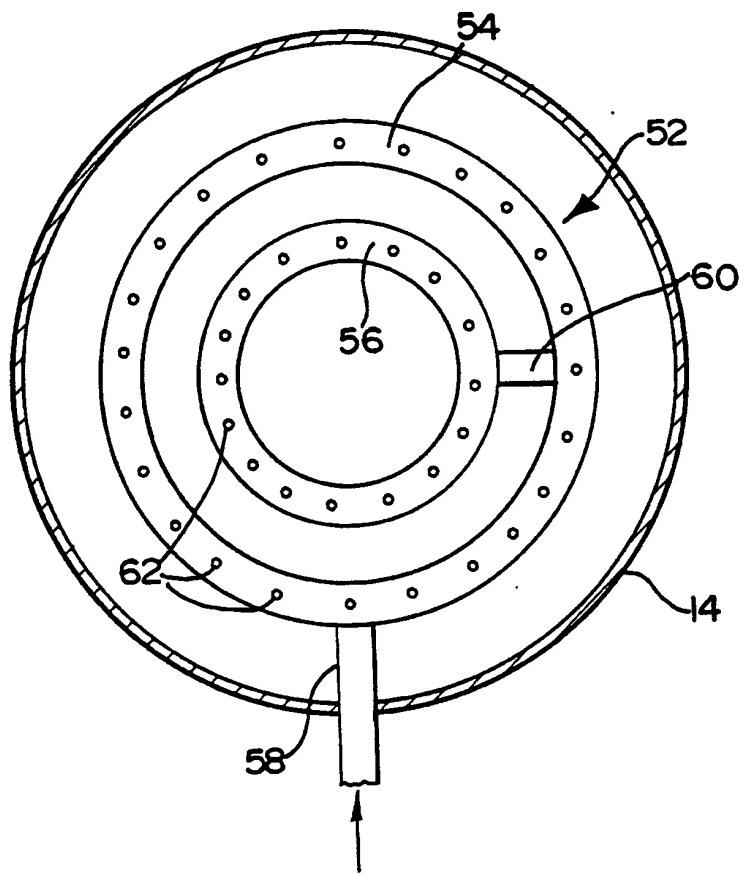


FIG 3

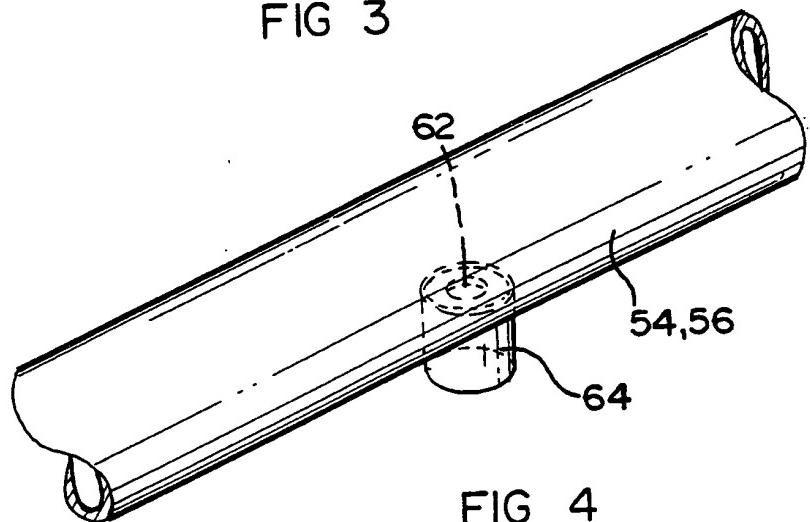
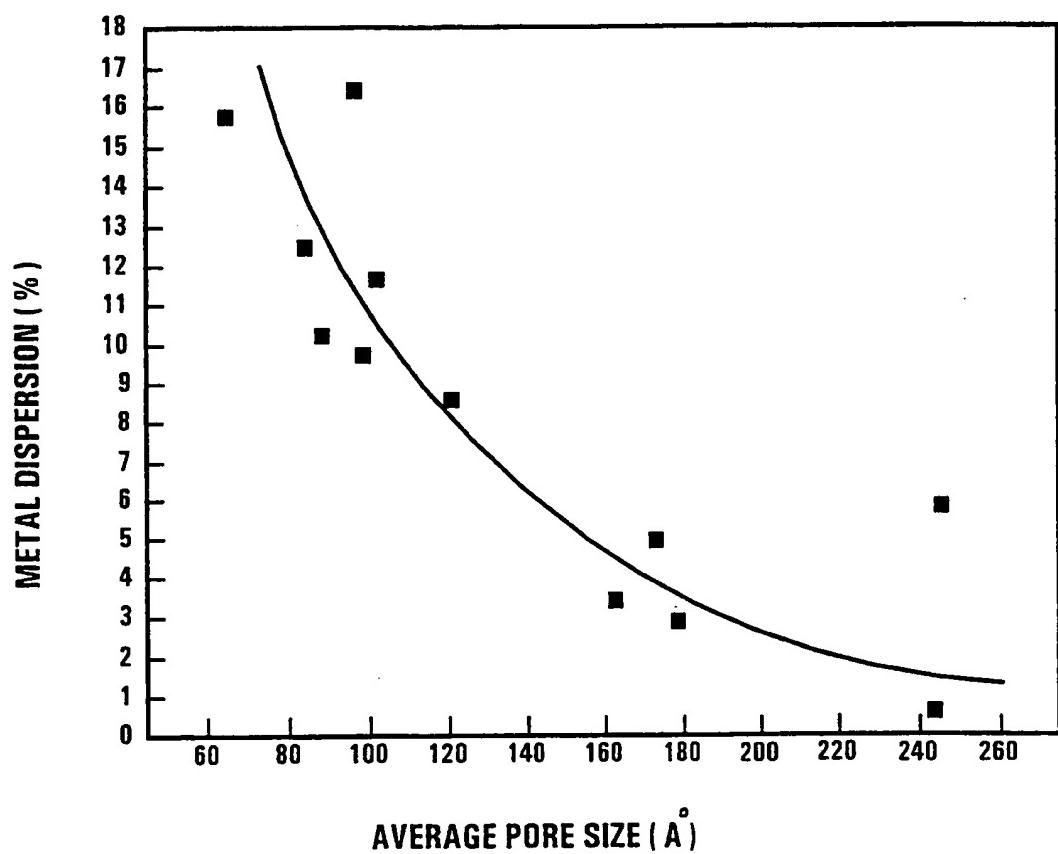
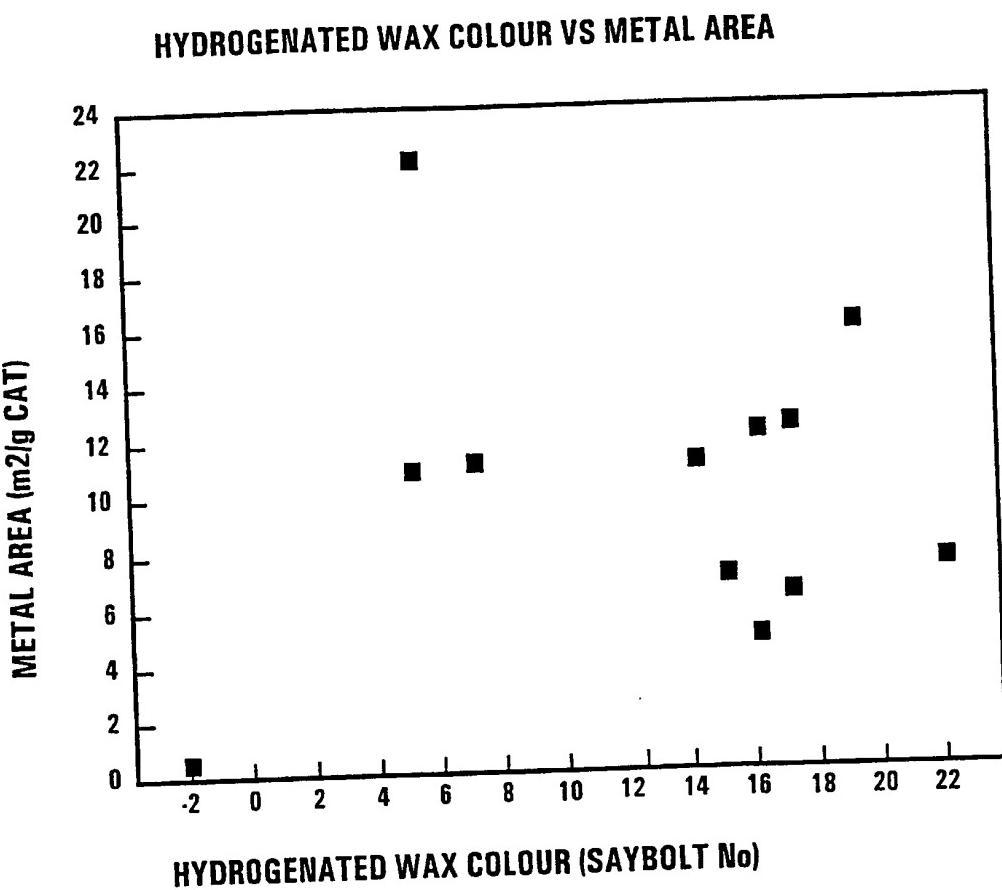


FIG 4

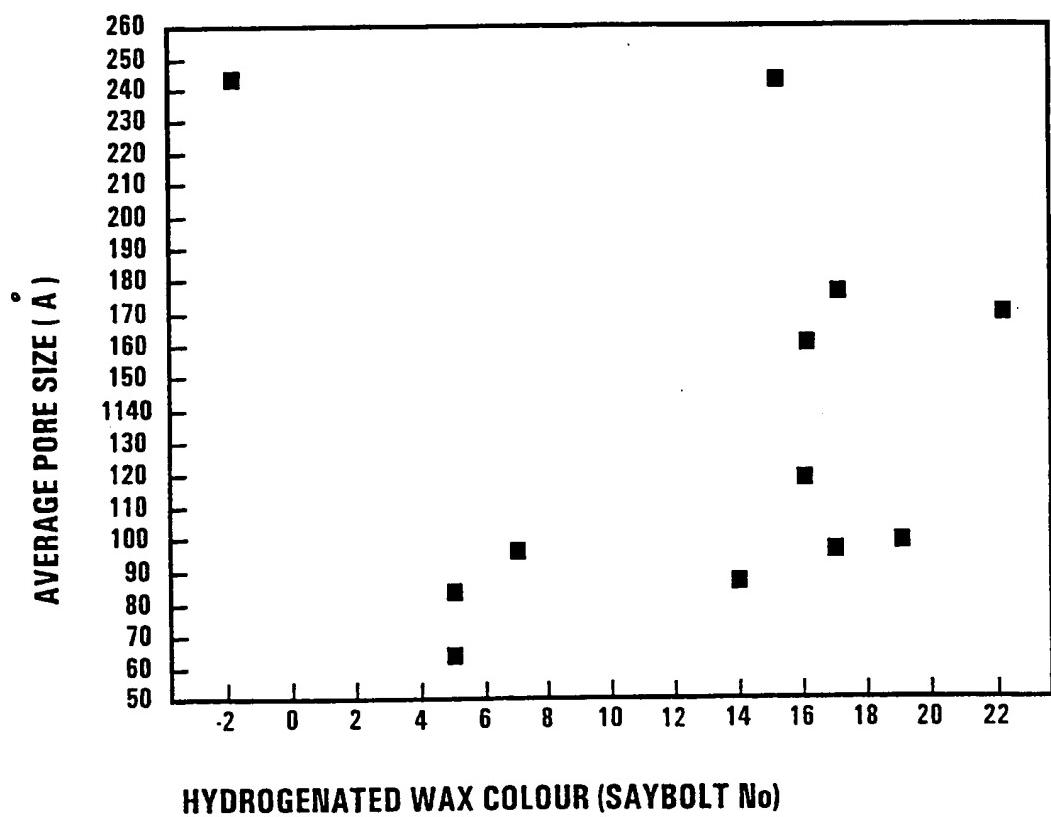
4/7

METAL DISPERSION VS AVERAGE PORE SIZE**FIG 5**

5|7

**FIG 6**

6/7

HYDROGENATED WAX COLOUR VS AVERAGE PORE SIZE**FIG 7**

7|7

**HYDROGENATED WAX COLOUR VS
METAL AREA * (AVG PORE DIAMETER)²**

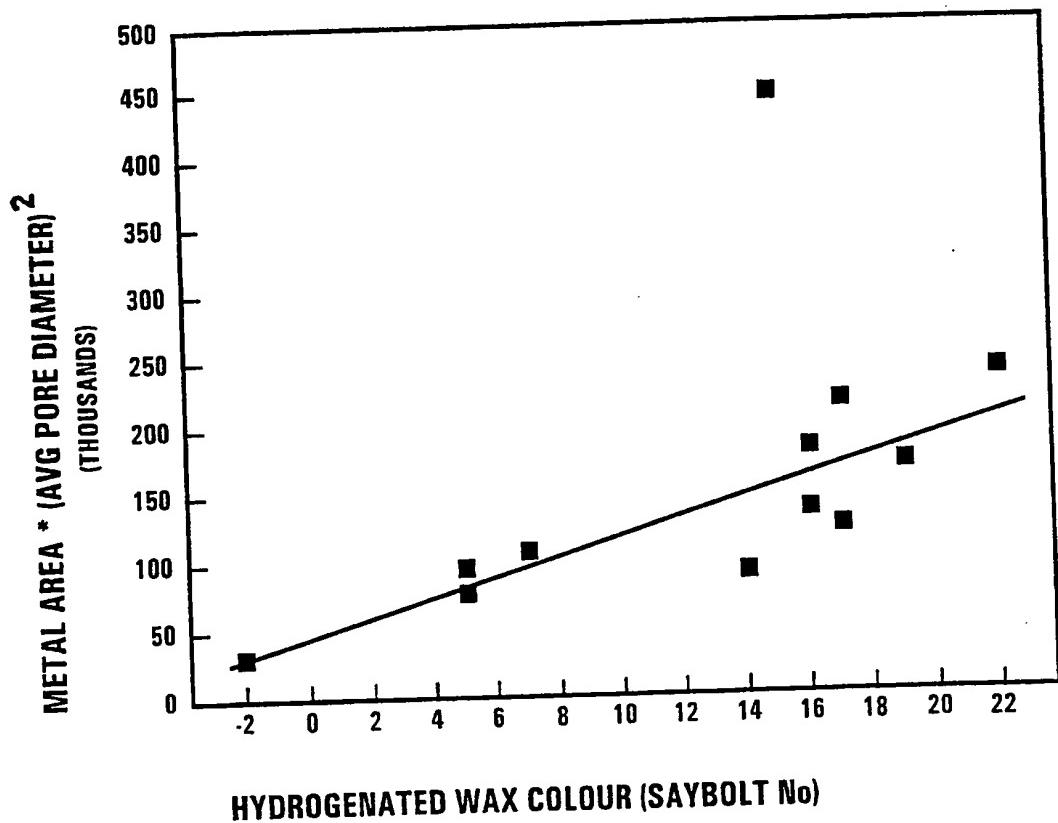


FIG 8



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | | |
|--|--|--|---|
| (51) International Patent Classification ⁶ : C10G 45/16, B01J 8/22, C07C 5/03 B01J 23/755, 37/02 | | A3 | (11) International Publication Number: WO 98/37168 |
| | | | (43) International Publication Date: 27 August 1998 (27.08.98) |
| (21) International Application Number: PCT/GB98/00409 | | (74) Agent: ABLEWHITE, Alan, James; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB). | |
| (22) International Filing Date: 10 February 1998 (10.02.98) | | | |
| (30) Priority Data: 97/1463 20 February 1997 (20.02.97) ZA 98/0586 23 January 1998 (23.01.98) ZA | | (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). | |
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| | | (88) Date of publication of the international search report: 5 November 1998 (05.11.98) | |
| (54) Title: CATALYST AND PROCESS FOR THE HYDROGENATION OF HYDROCARBONS | | | |
| (57) Abstract | | | |
| <p>A process for hydrogenating long chain hydrocarbons comprises continuously feeding a feedstock (24) comprising long chain hydrocarbons into a slurry bed (12) comprising a slurry of catalyst particles in a slurring liquid. The slurry bed is contained in a reaction zone (30) at a low level (24). A hydrogenation component is fed continuously (22) into the slurry bed, at a low level. The hydrogenation component is allowed to react with the feedstock, to hydrogenate the feedstock, as the feedstock and hydrogenation component pass upwardly through the bed (30). Hydrogenated long chain hydrocarbons are withdrawn from the reaction zone at a high level, (26) as a hydrogenated product. Any excess hydrogenation component is withdrawn from the reaction zone at a high level (48). The catalyst particles may have a size distribution between 1 and 250 microns. The catalyst may consist of a nickel component impregnated in a subatmospheric environment or a particulate alumina or silica carrier.</p> | | | |
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INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/GB 98/00409

| | |
|-------------------------------------|--|
| A. CLASSIFICATION OF SUBJECT MATTER | IPC 6 C10G45/16 B01J8/22 C07C5/03 B01J23/755 B01J37/02 |
|-------------------------------------|--|

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10G B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| Y | WO 96 12778 A (SHELL INT RESEARCH ; PRISTON ROBERT ANTHONY JOHN (NL); HOEK AREND () 2 May 1996 see abstract see page 3, line 4 - line 13 see page 4, line 4 - line 34 see page 9, line 21 - page 10, line 33 see examples see claims --- US 3 817 856 A (AARON S ET AL) 18 June 1974 see abstract; figures see column 2, line 6 - line 72 see claims --- US 5 308 476 A (BUTTKE ROBERT D ET AL) 3 May 1994 --- -/- | 1-8, 24, 25, 28 |
| Y | | 1-8, 24, 25, 28 |
| A | | |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

24 August 1998

Date of mailing of the international search report

10.09.1998

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-----------------------|
| A | US 4 624 968 A (FIATO ROCCO A ET AL) 25 November 1986 --- | |
| A | EP 0 736 326 A (SASTECH LTD) 9 October 1996 see page 2, line 5 - line 36 see claims --- | 9-23,26, 27 |
| A | US 4 861 746 A (OISHI YASUYUKI ET AL.) 29 August 1989 see abstract see column 3, line 23 - line 60 see claims ----- | 9-23,26, 27 |

INTERNATIONAL SEARCH REPORT

Int'l application No.

PCT/GB 98/00409

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims : 1-8, 24, 25, 28
A process for hydrogenating long chain hydrocarbons in a slurry bed reactor
2. Claims : 9-23, 26, 27
A process for the preparation of a catalyst

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Application No

PCT/GB 98/00409

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
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